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# NMR MEASUREMENTS ON HEATED OIL SHALES

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## INTRODUCTION

Many studies have been conducted in the past on various aspects of oil shale conversion; however, none have adequately addressed the basic chemistry involved during kerogen thermal decomposition (1). Instead, most of the studies have been concerned with the rate of kerogen conversion to products and average activation energies associated with the processes. Typically kerogen conversion is found to be a first order rate process and these data are used to provide a global or macroscopic description of kerogen conversion. The reason why structural information has not been obtained in previous work is that suitable analytical techniques have not been developed to provide such information. Now such techniques can provide information about the structure of kerogen and how the structure changes during heating. The most important technique is nuclear magnetic resonance (NMR) cross polarization (CP) with magic angle spinning (MAS).

In this paper, CP/MAS $^{13}C$ NMR techniques, with and without interrupted decoupling have been employed to measure changes in the organic carbon distribution of oil shales upon heating. The results suggest the potential of solid state $^{13}C$ NMR techniques for understanding the reaction chemistry during oil shale thermal decomposition.

## EXPERIMENTAL

A rich, 72 gallons per ton (GPT) oil shale was used for this study. Samples for NMR analyses were prepared by interrupting the heating schedule of the standard Fischer Assay when the retort reaches intermediate temperatures of 400°, 425° and 450°C. A fourth experiment corresponds to interruption of the Fischer Assay immediately upon reaching the maximum temperature of 500°C. Identical samples of 72 GPT oil shale were used in each of these experiments. The retorted shale from the standard Fischer Assay of the feed material was used as a fifth sample for comparison with the partially retorted materials. The Fischer Assay is not designed for quenching the retorting when the experiment is interrupted and no special cooling provisions were incorporated into the apparatus for these experiments. As a result, no kinetic information was derived from these experiments.

$^{13}C$ NMR measurements were made at 15 MHz $^{13}C$ frequency, 1-ms contact time and 1-s repetition rate. Interrupted decoupling spectra were recorded at a 75-μs interrupt time.

## RESULTS AND DISCUSSION

The preliminary experiments have provided samples which qualitatively represent the expected gradation in shale properties with increasing temperature and residence time. The experimental yields are listed in Table I along with the elemental compositions of the product shale samples.

The oil and gas yields increase with temperature and residence time, while the water yield remains constant within experimental error. The water yields reflect the production of essentially all bound water below 400°C. The concentration of the principal elements decreases in the shale with the increase in oil and gas yields. Random fluctuations in the carbonate carbon content probably reflect inconsistencies in the mineral composition of the samples.

The CP/MAS $^{13}C$ NMR spectra (Figure 1) for the shale samples indicate a decrease in the aliphatic carbon content with increasing oil yield. This observation is consistent with previous studies which indicate that the oil and gas production are primarily due to aliphatic carbon conversion (2). However, the spectrum of the 450°C sample shows some broadening with the appearance of a shoulder at 19 ppm and some aliphatic carbon remains in the retorted shale from the standard Fischer Assay. These observations suggest that the aliphatic carbon in the partially retorted samples has a higher concentration of short chain alkyl substituents. The rich oil shale shows a tendency to coke in the Fischer Assay and the residual aliphatic carbon may reflect partial coking

where the aromatization is incomplete.

TABLE I

PRODUCT ANALYSES

| Yields | Temperature at Interruption 400°C | 425°C | 450°C | 500°C | Fischer Assay |
|---|---|---|---|---|---|
| Oil, % w | 0.6 | 2.8 | 11.1 | 27.1 | 27.5 |
| Gas, % w | 0.6 | 1.6 | 2.5 | 4.9 | 6.3 |
| Water, % w | 2.2 | 2.4 | 2.6 | 2.2 | 2.2 |
| Composition of Spent Shale Samples | | | | | |
| Carbonate C, % w | 3.6 | 6.4 | 8.0 | 6.3 | 6.0 |
| Organic C, % w | 29.7 | 24.2 | 17.7 | 5.9 | 6.1 |
| Hydrogen, % w | 4.0 | 3.5 | 2.6 | 0.4 | 0.3 |
| Nitrogen, % w | 1.0 | 0.9 | 0.8 | 0.5 | 0.5 |
| Sulfur, % w | 1.6 | 1.3 | 1.1 | 0.5 | 0.5 |

TABLE II

AROMATICITY MEASUREMENTS

| Interruption Temperature | Carbon Aromaticity Shale | Oil | Hydrogen Aromaticity Oil | Product Oil Specific Gravity | H/C Ratio |
|---|---|---|---|---|---|
| 400°C | 0.30 | 0.12 | 0.035 | - | - |
| 425°C | 0.33 | 0.24 | 0.045 | - | 1.74 |
| 450°C | 0.39 | 0.26 | 0.041 | 0.892 | 1.74 |
| 500°C | 0.73 | 0.31 | 0.051 | 0.907 | 1.65 |
| Fischer Assay | 0.79 | 0.29 | 0.056 | 0.909 | 1.66 |

The aromatic carbon bands in the CP/MAS $^{13}C$ NMR spectra are narrower at the higher temperatures and longer residence times. This observation suggests that the aromatic carbon becomes less substituted and more condensed. Similar behavior is observed for coals as a function of rank (3, 4). The partially retorted samples resemble oil shales of different "rank". In this analogy, the "rank" is artificially produced by heating to high temperatures for short periods of time as compared to slow heating over geologic time.

Liquid-state NMR measurements of the product oils are consistent with the solid-state CP/MAS $^{13}C$ NMR results. Both the $^{13}C$ and 1H aromaticity values increase at the higher temperatures and longer residence times. These data represent a shortening of the aliphatic carbon chains. Also, some dehydrogenation reactions may conceivably occur at the higher temperatures. An observed increase in the oil specific gravity and a corresponding decrease in the H/C atomic ratio support the aromaticity data by NMR. These data are compared with the NMR measurements in Table II.

The partially retorted shale samples are also used to test interrupted decoupling techniques for supplementing CP/MAS in the application of $^{13}C$ NMR to solid shale samples. For these experiments, the $^{13}C$ NMR spectra are interrupted at 75 μs. The interrupted decoupling spectra are not scaled to zero time as suggested by Murphy et al. (5, 6) for quantitative measurements. Thus, in this paper the interrupted decoupling spectra are used for qualitative assessments. The interrupted decoupling technique discriminates between carbon with hydrogen directly attached and carbon which is not directly bonded to hydrogen. However, the technique does not completely suppress methyl carbon contributions to the spectra. In this preliminary application, the carbonyl region of the spectra (> 170 ppm) is enhanced and some shoulders in the spectra suggest the presence of phenolic carbon (150-160 ppm). The center of the aromatic carbon region in the spectra is shifted upfield and becomes narrower with increasing temperature and residence time. These observations suggest a trend from substituted quaternary aromatic carbon at low temperatures to more polycondensed quaternary aromatic carbon at higher temperatures. The residual aliphatic carbon in the fully retorted shale sample is not present in these spectra, suggesting that these carbons are secondary and tertiary aliphatic carbons.

While the NMR data for the heated shales are preliminary and qualitative, the chemical

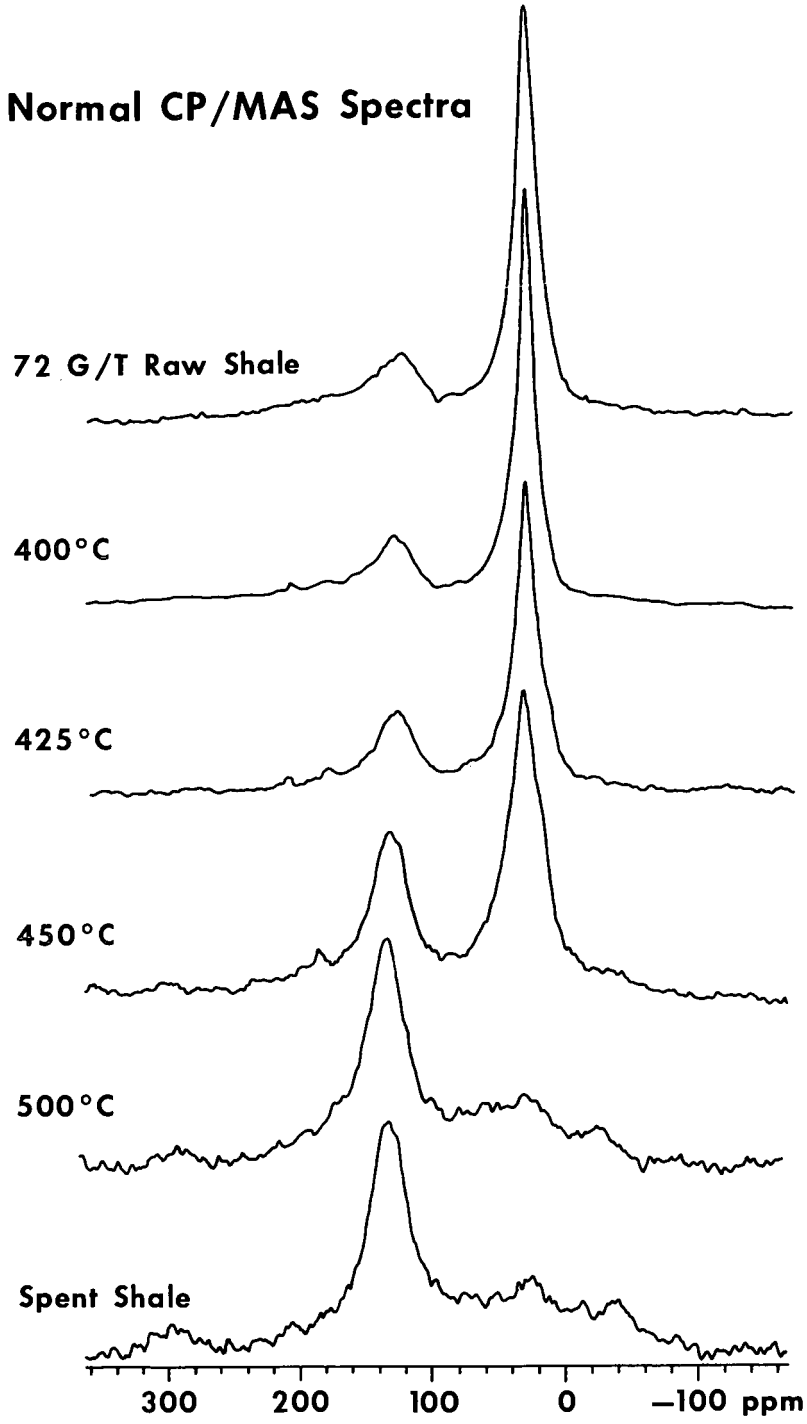


Figure 1. CP/MAS $^{13}C$ NMR Spectra of heated Colorado oil shale.

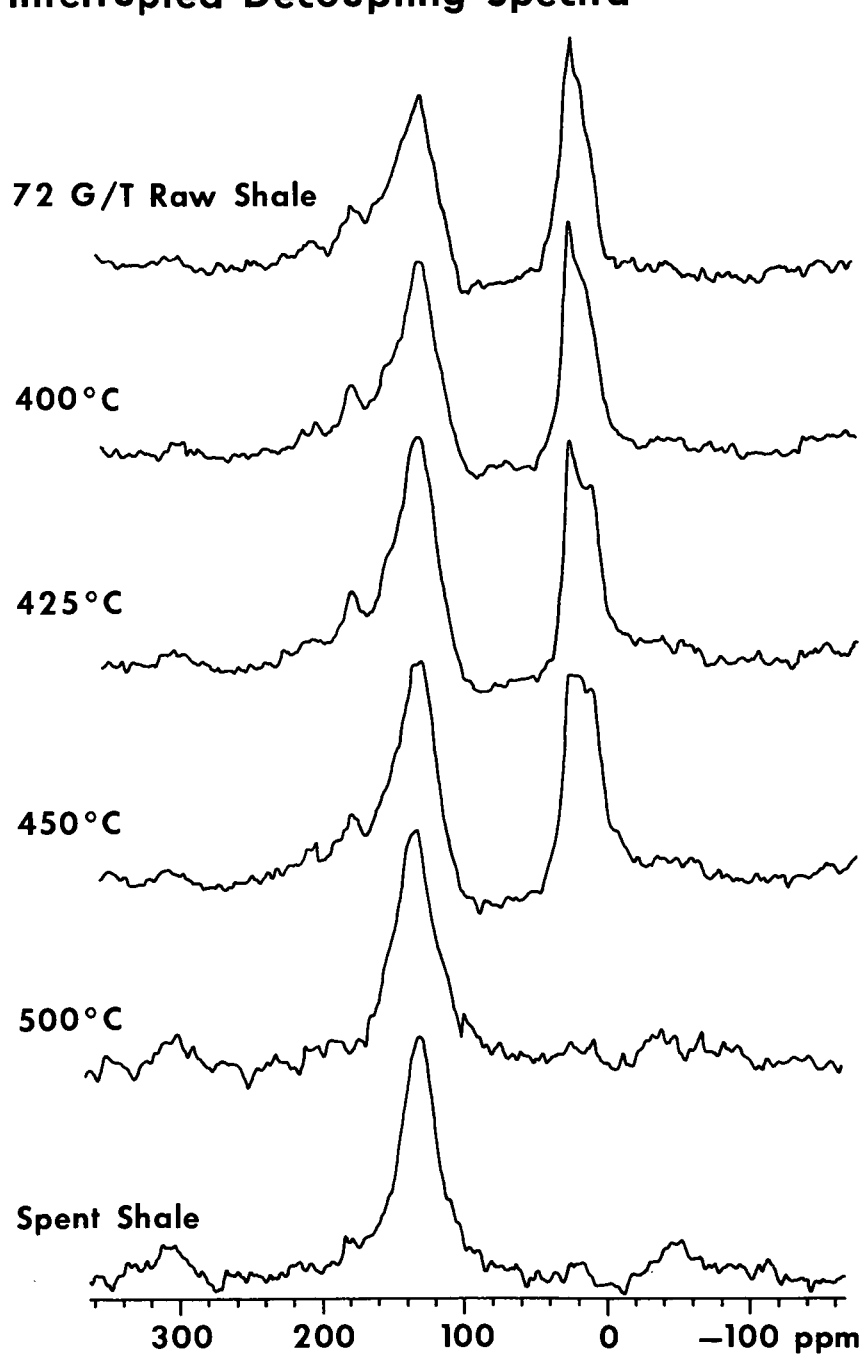


Figure 2. Interrupted decoupling spectra of heated Colorado oil shale. The interrupt time is 75 μs.

information obtainable by CP/MAS $^{13}C$ NMR techniques make them attractive for the study of oil shale reaction kinetics. More detailed studies are in progress.

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